

Occurrence and Distribution of Arsenic in Soils and Plants

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Inorganic arsenicals have been used in agriculture as pesticides or defoliants for many years and, in localized areas, oxides of arsenic have contaminated soils as a result of fallout from ore-smelting operations and coal-fired power plants. Use of inorganic arsenicals is no longer permitted in most agricultural operations, and recent air pollution controls have markedly reduced contamination from smelters. Thus, this paper will concentrate on the effect of past applications on arsenic accumulation in soil, phytotoxicity to and uptake by plants as influenced by soil properties, and alleviation of the deleterious effects of arsenic.

Once incorporated into the soil, inorganic arsenical pesticides and arsenic oxides revert to arsenates, except where the soil is under reducing conditions. The arsenate ion has properties similar to that of orthophosphate, and is readily sorbed by iron and aluminum components. This reaction greatly restricts the downward movement (leaching) of arsenic in soils and the availability of arsenic to plants.

Several methods of estimating plant available arsenic in soils have been developed. They involve extraction of the soil with reagents used to estimate phosphorus availability. This extractable arsenic is reasonably well correlated with reduced plant growth by, and plant uptake of arsenic. For most plants, levels of arsenic in the edible portion of the plant are well below the critical concentration for animal or human consumption, even when severe phytotoxicity occurs.

Alleviation of arsenic phytotoxicity has been attempted by increasing the soil pH, by use of iron or aluminum sulfate, by desorbing arsenate with phosphate and subsequent leaching, and by cultural practices such as deep plowing. Only limited benefits have accrued from these procedures the cost of which is often prohibitively high. Since attempts to reduce arsenic toxicity have not been very successful, its excessive accumulation in soils should be avoided.

Introduction

Inorganic arsenicals were originally used in agriculture for the control of various insect pests such as the Colorado potato beetle, codling moth in apples, horn worm in tobacco, and boll weevil in cotton. Control often required the application of considerable quantities of lead or calcium arsenate or cuprous arsenite (1). More recently, arsenic trioxide has been widely used as a soil sterilant and sodium arsenite for aquatic weed control and as a defoliant to kill potato vines prior to harvest (2-5).

Arsenical sprays have also been used to control the ripening of grapefruit and Valencia oranges (6).

Arsenic is one of the few metal elements for which recent developments indicate a decreasing rather than increasing concern over concentrations in the food chain. The primary reason for this stems from the banning of sodium arsenite as a defoliant and the replacement in fruit orchards of substantial quantities of lead arsenate by carbamates and organic phosphates (7). Organic arsenicals are now used where required, and are applied at much lower rates than the inorganic arsenic compounds. The net result has been a drastic lowering of the amount of arsenic reaching the soil. Poultry are often fed 3-nitro-4-hydroxyphenylarsonic acid, but the arsenic from their manure does not accumulate in corn grain grown on soils receiving up to 600 tons manure/ha and does not seem to pose a hazard (8).

With this in mind the objectives of this paper will

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be to review arsenic chemistry in the soil in relation to its immobilization and methods for its determination which have prognostic value in terms of plant uptake and phytotoxicity; to define as far as possible the conditions under which arsenic becomes phytotoxic and potentially hazardous to humans and animals ingesting plant material from treated soils; and finally, to evaluate methods of decreasing the arsenic hazard in contaminated soils.

Arsenic Chemistry in Soils

Arsenic is ubiquitous in nature, occurring in most soils and rocks in detectable quantities. Concentrations of arsenic in uncontaminated soils range from 0.2 to 40 ppm. No clearly defined relationship exists between the arsenic content of soils and the parent material or climatic conditions under which the soils were formed. In uncontaminated soils the level of arsenic is not sufficiently high to cause phytotoxicity and does not therefore represent a health hazard.

Table 1. A comparison of As levels in As-treated and uncontaminated soils in North America.^a

Sampling site	Total As content, ppm		Crop
	Uncontaminated soil	Treated soil ^b	
Colorado	1.3-2.3	13-69	Orchard
Florida	8	18-28	Potato
Idaho	0-10	138-204	Orchard
Indiana	2-4	56-250	Orchard
Maine	9	10-40	Blueberry
Maryland	19-41	21-238	Orchard
New Jersey	10.0	92-270	Orchard
New York	3-12	90-625	Orchard
North Carolina	4	1-5	Tobacco
Nova Scotia	0-7.9	10-124	Orchard
Ontario	1.1-8.6	10-121	Orchard
Oregon	2.9-14.0	17-439	Orchard
Washington	3-32	4-103	Orchard
	6-13	106-830	Orchard
	8-80	106-2553	Orchard
Wisconsin	4-13	48	Orchard
	2.2	6-26	Potato

^aData of Walsh and Keeney (9).

^bThese are results from soils that had been repeatedly treated with an As pesticide or defoliant. Soils treated experimentally are not included.

Soils from land repeatedly treated with inorganic arsenicals contain levels of arsenic often 10- to 100-fold those of untreated areas (Table 1). Use of arsenicals as insecticides usually results in higher concentrations of arsenic in the soil than when they are used as defoliants.

Arsenic chemistry is in many ways very similar to that of phosphorus, especially in aerated systems, and it is generally held that the arsenate ion

closely resembles orthophosphate. However, arsenic is more labile than phosphorus, and unlike phosphorus it can undergo valence state changes over the range of redox conditions likely to be found in soils and biological systems (10). Also, it apparently does not accumulate in organic forms in soils. Under strongly reducing conditions elemental arsenic (As₄) and arsine (AsH₃) (-III) are the stable forms. In less reduced environments, such as those in flooded soils, the relatively toxic arsenite (MAsO₂) (+III) can be formed. However, in aerated soils, arsenate (MAsO₄) (+V) predominates. The above valence states can form compounds containing the C-As bond and are readily interconverted by soil microorganisms which do not seem to utilize the energy produced by oxidation for growth (11, 12). Arsenite added to a well-drained soil having significant biological activity is oxidized in a matter of a few days (13). In reduced environments such as sediments, arsenate is reduced through arsenite to dimethylarsinic acid, which is extremely toxic (12). Evidence exists that this compound may be more ubiquitous than previously realized due to lack of methods for its detection and estimation (14). Soluble arsenic has been observed to increase in flooded rice soils (15). This was attributed largely to the reduction of ferric to ferrous iron, but the possibility of arsenite formation was not ruled out.

The level of soluble arsenic in soils is determined by the relative arsenic sorptivity of soil components, chiefly iron and aluminum compounds. For example, all of the arsenic added to soils is removed by treatment with oxalate, which also removes iron and aluminum bound in allophanic materials and hydrous oxides (16). These are now termed short-range order iron and aluminum components. Hydrous ferric oxides have been shown to be effective in sorption of arsenate (17). The importance of adsorption is further supported by the decrease in extractable arsenic from arsenic-amended soils with time (9, 16, 18) and the apparent ability of phosphate to replace arsenate from soils (19, 20). The high proportion of sorbed arsenate extractable by neutral salts (16) also indicates that it is weakly sorbed by soils relative to phosphate.

Although arsenic can form moderately insoluble salts with ferric iron and aluminum, the previous observation on the mobility of arsenate in soils would indicate that discrete arsenate compounds do not form in soils, and arsenate is retained in soils by sorption mechanisms.

As a first approximation, the sorptive capacity of a soil for an ion such as arsenate is a function of its surface area, and hence of its clay content (3, 16, 18, 21-23). Thus, arsenic would be expected to be more labile in low clay (sandy) soils, explaining ob-

servations that arsenic phytotoxicity is more likely on sandy than on fine-textured soils (24–26) and that arsenate can leach through the profile of sandy soils (27).

Soil Arsenic and Plant Growth

Plant growth stimulation has often been observed as a result of low levels of arsenic additions to soils, despite the fact that it is not considered as an essential element for plant growth. Two mechanisms have been proposed to explain this stimulation, the one being presumed to be similar to that obtained by other pesticides (e.g., 2, 4-D) at sublethal dose levels (18) and the other being due to the displacement of phosphate by arsenate from soil surfaces, thereby increasing phosphate availability (27). Depression of plant growth usually occurs at higher levels of arsenic application and is particularly severe when treated orchards are removed and the land replanted to an agronomic or horticultural crop (3, 28).

Plants vary considerably in their tolerance to high levels of soil arsenic. Potatoes, cabbage, tomatoes, carrots, tobacco, rye, Sudan grass, and grapes are highly tolerant; strawberries, corn, beets, and squash are moderately tolerant; and onions, cucumbers, and legumes have low tolerance (24, 26, 29).

Plants take up arsenic from the solution phase of soils and therefore measures of labile forms should be better related to plant uptake than the total arsenic content when soils with widely varying properties are compared (21, 26). The labile forms are usually measured by extracting the soil with hot water, dilute acids, salt solutions or complexing agents. These remove a certain reproducible proportion of the total arsenic which happens to be soluble in the particular reagent. A summary of a few recent studies (Table 2) shows the "critical" level of arsenic at which a yield depression might be expected is influenced by plant species and varies with differing soils. Arsenic extracted by many of these extractants, such as Bray P-1 (0.025N HCl + 0.3N NH_4F), 0.5N NaHCO_3 , or 0.05N HCl plus 0.025N H_2SO_4 are satisfactorily related to the amount of arsenic available to the plant (18, 24, 25). Examples of correlation coefficients between yields of a number of crops and arsenic extracted by various methods are presented in Tables 3 and 4. Even though water-soluble and total arsenic can satisfactorily predict phytotoxicity in certain cases, soil testing laboratories can more conveniently use the "available arsenic" extractants because they are routinely used to estimate available P.

Bioaccumulation of arsenic would be hazardous

Table 2. Levels of soil As at which significant yield depressions occur.^a

Crop name	Soil type	Level of As at which significant yield depressions occurred, ppm		
		Total As	Water soluble As	Available As
Blueberry	Colton loamy sand	44	6	—
Cotton	Amarillo fine sandy loam	—	8	—
Cotton	Houston Black clay	—	28	—
Soybean	Amarillo fine sandy clay	—	3	—
Soybean	Houston Black clay	—	12	—
Potatoes, sweet corn	Plainfield loamy sand	68	—	22 ^b
Snap beans, peas	Plainfield loamy sand	25	—	10 ^b
Corn	(Average of 13 soils)	85	—	10 ^c

^a Data of Walsh and Keeney (9).

^b Extracted with Bray P-1 (0.25N HCl plus 0.3N NH_4F).

^c Extracted with either 0.5N NaHCO_3 or 0.05N HCl plus 0.025N H_2SO_4 .

Table 3. Correlation coefficients for yield vs. extractable arsenic.^a

Soil	Crop	Extractant ^b		
		H_2O	HCl	NH_4Cl
Amarillo	Soybeans	-0.943	-0.915	-0.914
Houston	Soybeans	-0.968	-0.931	-0.938
Amarillo	Cotton	-0.951	-0.830	-0.960
Houston	Cotton	-0.954	-0.895	-0.918

^a Data of Stevens et al. (27).

^b All of the correlation coefficients are significant at the 0.05 probability level.

Table 4. Relationships between total or extractable soil As and yield of vegetable crops.^a

As fraction	Crop ^b			
	Potatoes	Peas	Snap beans	Sweet corn
NH_4OAc	-0.91	-0.85	-0.73	-0.91
Bray P-1	-0.91	-0.88	-0.77	-0.93
Total	-0.92	-0.87	-0.75	-0.93

^a Data of Jacobs (26).

^b All correlation coefficients significant at the 0.01 probability level.

to humans and animals because of its possible relationship to cancer, arteriosclerosis and chronic liver disease (30). Fortunately, the edible portions of plants seldom accumulate dangerous levels of arsenic because phytotoxicity occurs before such levels are reached. The highest concentrations of arsenic

are found in plant roots, intermediate levels in vegetative tissue and the lowest levels in reproductive tissue (Table 5). Toxicity to animals or humans usually is due to the ingestion of surface residues of arsenic on plant material. The U. S. Public Health Service tolerance level for arsenic in edible plant material is 2.6 ppm and most products grown on arsenic-treated soils would comply with this requirement (32, 33). Even though the arsenic additions reported in Table 5 caused yields to decrease to approximately half of those obtained on unamended soil, the tolerance level was not exceeded in the above-ground portions of the plants (31).

Table 5. Comparison of the arsenic content and distribution in plants grown on untreated and arsenic-treated soil.^a

Crop	Plant part	Arsenic content, ppm fresh weight basis	
		Check plots	Arsenic plots ^b
Peas	Seeds	0.01	0.18
	Pods	0.05	0.88
	Vines	0.12	2.14
Beans	Seeds	0.01	0.07
	Pods	0.27	0.79
	Leaves	0.21	1.92

^aData of McPhee et al. (31).

^bThis soil contained approximately 150 ppm As.

Tobacco seems to be an exception to this general rule. Concentrations as high as 14 ppm arsenic in flue-cured leaves of tobacco grown on a soil which received 54 kg of arsenic/ha (as lead arsenate) have been obtained (23). This poses an additional health hazard for smokers. There is evidence to suggest a relationship between the arsenic content of cigarettes and lung cancer (34). One might expect root crops (e.g., potatoes) to contain high levels of arsenic when grown in treated soils. However, this is not the case, as most of the arsenic (2 to 3 ppm) is confined to the peelings, and much of this arsenic probably is due to minute quantities of contaminated soil adhering to the tuber surface (27, 35). Little arsenic accumulates in the reproductive tissues, and hence seed crops would not exceed the arsenic tolerance level even where phytotoxicity reduced growth by 50% (24).

In general, available soil arsenic is well correlated with arsenic concentration in the whole plant, but because plants tend to exclude arsenic from seeds and fruits, soil tests for available arsenic would not be reliable predictors of the concentration likely to be found in edible plant tissue (24).

The contamination of the aerial portions of plants with arsenic-containing dust from treated soil can occur (26). This possibility casts some doubt on published values for arsenic uptake in cases where steps were not taken to remove adsorbed soil particles from plant organs (26).

Arsenic Toxicity in the Future

Because the use of inorganic arsenicals on nearly all vegetable and agronomic crops has been banned since 1968 in the U. S. (7), the major problem to be addressed in the future is the reclamation and restoration of arsenic-contaminated soils to their optimal production level. A number of possibilities exist in this regard.

As pointed out earlier, the available arsenic level in many soils slowly decreases with time, although no information is available to predict how long would be required for the available arsenic to decrease to background concentrations. Another approach which has been proposed is to add sufficient phosphate to the system to depress arsenate uptake by the plant. This has been shown to be true in solution cultures (36, 37), but in soil systems the results are less clear because phosphate and arsenate compete for the same sorption sites in soil. Results have been reported where phosphate additions have either had no effect (38) or increased arsenic toxicity as a result of displacement of arsenate from sorbed sites by phosphate into solution increasing its availability (19, 20). Thus phosphate additions to decrease arsenic phytotoxicity appear to be of little value. Since arsenate is sorbed by iron and aluminum compounds, another obvious approach is to add iron or aluminum salts, along with sufficient lime to neutralize the acidity produced, to increase the surfaces potentially available for arsenate sorption. While this is theoretically feasible, such large amounts of iron and aluminum need to be added that this approach is uneconomical.

Deep plowing to dilute the arsenic concentration in the surface soil and expose the arsenate to more sites for fixation has been suggested as one of the most economical methods of decreasing toxicity (17, 39). Arsenic toxicity has sometimes been lessened by growing and plowing under tolerant cover crops such as rye or Sudan grass (22). Because excessive arsenic in some fruit trees induces zinc deficiency, foliar sprays of zinc sulfate or zinc chelates have in some cases helped to overcome arsenic toxicity. Concurrent high nitrogen applications to the soil also were beneficial (40-42).

In soils in which added phosphate desorbs arsenate, deliberate leaching of the soil after phosphate addition may be a viable approach to removing arsenic from the root zone (20). This would be particularly true of sandy soils which have been shown to desorb arsenate and are easy to leach (19, 20, 27). Work in the Netherlands has indicated that in humid regions leaching of arsenic can result in considerable attenuation of phytotoxicity. A half-life value for arsenic in soil of 6.5 ± 0.4 yr was calculated from this study (42).

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